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Studies on the nature of active species in $W(CO)_6/CCl_4/h\nu$ system as applied to metathesis polymerisation reactions

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Abstract

Irradiation of $W(CO)_6$ in CCl_4 generates an 'active species' which has the ability to polymerise alkynes and strained cyclic olefins via a metathesis pathway. The precipitate formed after 2 h of irradiation is active for polymerisation. The involvement of metal carbene in the polymerisation of norbornene was proved by in situ ^{1}H-NMR study and by the end-capping reaction. IR studies showed the presence of carbonyl and chlorine ligands around the tungsten centre. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metathesis polymerisation; Photolysis; $W(CO)_6$; CCl_4; Phenylacetylene; Norbornene

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1. Introduction

The photochemically activated catalyst system $W(CO)_6/CCl_4/h\nu$ has been exploited by various groups for metathesis of olefins [1–3]. Reports are also available for its use in homo- and co-polymerisation of alkynes and strained cyclic olefins [4–6]. Although intervention of metallacarbene complexes in such metathesis reactions is generally assumed, the mechanism of formation of these moieties has not been completely elucidated. Garnier et al. [7] have suggested the formation of a tungsten compound with a dichlorocarbene ligand of the formula $(CO)_2Cl_3W{=}CCl_2$ by an indirect method based upon the reaction product of 1-ethoxynorbornene with pre-irradiated $W(CO)_6$ in CCl_4. However, the claim that irradiation of $W(CO)_6$ in CCl_4 leads to an active species containing dichlorocarbene ligand was subsequently questioned [8]. Here the authors allege that a polymeric tungsten compound of unknown composition containing no carbonyl ligand is the catalytically active species. In this paper, we have looked at the nature of the active species by employing this system as a metathesis polymerisation catalyst.

2. Experimental

The photolysis reactions were carried out in a photochemical reactor (Heber Scientific HEAOP System) using 350 nm wavelength low-pressure mercury lamps as the source. IR and far-IR spectra were obtained using a Shimadzu (model 470) IR spectrophotometer using PEG powder. ^{1}H-NMR spectra were recorded using a JEOL model GSX400 high-resolution spectrometer (400 MHz). Thermogravimetric analysis was done on a Perkin–Elmer Thermal Analyser (model TGA7) under nitrogen atmosphere. Molecular weights of the polymers were obtained using Waters gel permeation chromatography (GPC) with polystyrene standards as reference and THF as solvent. Catalyst preparation and polymerisation were carried out under a dry and oxygen-free nitrogen atmosphere. All transfers were performed in a nitrogen-filled glove bag or by standard syringe techniques under an oxygen-free atmosphere. The metal carbonyl, norbornene (NBE) and phenylacetylene (PA) were bought from Aldrich and were used as such. All solvents used were purified, dried and stored over molecular sieves.

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2.1. Generation of active species and polymerisation procedure

A 100 ml round-bottomed flask with a Teflon®-coated magnetic stirrer bar was flame dried, capped with a septum and cooled while purging with nitrogen. A calculated amount of $W(CO)_6$ was transferred into the flask in a glove bag filled with nitrogen, 20 ml of dry, deaerated CCl_4 was syringed into it and the contents were irradiated for 2 h under nitrogen with stirring. The colourless solution turned deep blue, after which a calculated amount of monomer was added to the active species, the flask wrapped with aluminium foil and the contents stirred for 24 h at room temperature (r.t.). The reaction mixture was then poured into methanol to precipitate the polymer or the reaction mixture was centrifuged and the supernatant liquid with polymer containing the active metal centre was used for characterisation.

2.2. Study of the rate of consumption of $W(CO)_6$

A solution of appropriate concentration of $W(CO)_6$ in CCl_4 was irradiated with 350 nm light. Aliquots of 0.5 ml were withdrawn at regular time intervals and the infrared spectra of the samples were recorded in the region between 2500 and 1600 cm^{-1}.

2.3. Synthesis of p-phenylene divinyl linked copolymers (end-capping reaction)

Fifty equivalents of PA were polymerised with the active species (one equivalent) as generated above. The polymer in solution was treated with terephthalaldehyde and precipitated in methanol. The end-capped PPA was redissolved in CCl_4 and treated with a solution of polyNBE (50 equivalents of NBE polymerised as above) and stirred for another 12 h. The final polymer was precipitated in methanol and purified.

2.4. Observing the active species by ^1H-NMR spectroscopy

$W(CO)_6$ (0.186 g, 0.5 mmol) was transferred into the flask in a nitrogen-filled glove bag and 30 ml of dry, deaerated CCl_4 was syringed into the flask. This was irradiated for two hours and then NBE (five equivalents) was added and stirred for one more hour. The contents of the flask were reduced to one-sixth of its initial volume, transferred to an NMR tube via cannula and the ^1H-NMR spectrum of this solution was recorded.

3. Results and discussion

Since metal carbonyls show strong absorptions in the IR spectra, we decided to study the kinetics of consumption of $W(CO)_6$ in CCl_4, upon photolysis, by monitoring the terminal carbonyl absorption at 1975 cm^{-1}. As expected, there was a gradual decrease of the signal at 1975 cm^{-1} with time and it disappeared after an irradiation period of 1.5–2 h. Simultaneously another peak at 1806 cm^{-1} appeared within 15 min of irradiation but the increase in intensity of this peak was not proportional to the decrease in the intensity of the carbonyl peak. The areas under the 1975 cm^{-1} peak were used for the kinetic analysis. A plot of $\ln[a/(a-x)]$ versus time, for the initial 1 h of reaction gave a linear fit with a correlation of 93% and the rate constant (slope) was found to be 1.5×10^{-2} min^{-1}. The rate of consumption was also pseudo-first order for $W(CO)_6$.

Upon irradiation, the colourless $W(CO)_6$–CCl_4 solution first turned blue, then dark greenish–brown and finally into a dark brown suspension. The precipitate was separated from the supernatant by cannula — transferring the latter under nitrogen into another flask. The monomer (NBE or PA) was added to both (5 ml of CCl_4 was also added to the former) and stirred for 24 h. The reaction was then quenched by pouring into excess methanol. It was found that no polymer formed in the second instance. In order to check if CCl_4 as solvent was necessary to catalyse the reactions, we performed the following experiment. After generation of the active species, CCl_4 was removed under vacuum and replaced by dry, deaerated hexane. The monomer was then added, the mixture stirred for 24 h and the polymer

Table 1
Comparison of activity of $W(CO)_6/CCl_4/h\nu$ system under different reaction conditions

S.No	Reaction conditions	Percentage yield of the polymer	
		PPA	PNBE
1	Supernatant (after generation of active species)	1	0
2	Precipitate (wet, i.e. after generation of active species and removal of supernatant)	52	24
3	Precipitate (vacuum dried after generation of active species) in dry, deaerated hexane	7	<1
4	Active species as generated	66	29

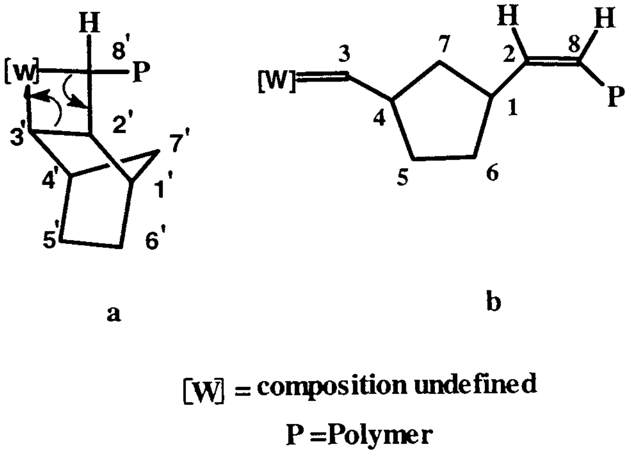


Fig. 1. Structure of the propagating species.

precipitated by pouring the reaction mixture into excess methanol. The results of the above experiments are given in Table 1. From the actual yields of the polymers obtained for both the monomers, it can be noted that the precipitate as generated was the most effective for giving maximum conversion.

In order to characterise the active species, the following attempts were made. The active species was generated as given earlier. The contents were centrifuged and the centrifugate was removed by cannula-transfer. The residue was washed 3–4 times with dry, deaerated hexane to remove unreacted $W(CO)_6$. The precipitate was used for further analysis. On examining its TGA, a weight loss of nearly 70% was found to occur at 120°C, showing that the species was not thermally very stable. In another experiment, the catalyst was generated as usual, ten equivalents of PA was added to this catalyst and after twelve hours the contents were centrifuged. The residue was tested for its ability to polymerise PA and no polymer formed even after 24 h. Hence it was concluded that the active species started the polymerisation and it was present in the polymer chain. The residue was then discarded and the solution of the polymer chain containing the active end was used for recording the IR spectrum. In the IR spectrum, we observed peaks at 1993, 1963 and 1912 cm^{-1} that could be ascribed to the M–CO group and the broad bands in the region 900–600 cm^{-1} and at 371 and 322 cm^{-1} could be assigned to W–Cl vibrations. This might point to the presence of chlorinated tungsten carbonyl centres in the solution, possibly as the active end of the growing polymer chain.

Furthermore, in this system though the active species is not well defined or well characterised, we attempted to follow the course of ring opening of NBE by NMR. For this study, the active species was generated as earlier and five equivalents of NBE, were added, stirred for 1 h and the ^{1}H-NMR was recorded for the reaction mixture. In addition to the peak of the solvent and that of the reference, several signals were seen which could be attributed to the structures shown in Fig. 1.

The ^{1}H-NMR spectrum of the proposed adduct is shown in Fig. 2 and the peaks are assigned as follows. The peak at δ 3.3 and a doublet at δ 3.8 are due to protons on C-3′ and C-8′ carbons. The peak at δ 2.1 is assigned to protons attached to carbons, C-1′ and C-4′. These peaks are characteristic of a metallacyclobutane intermediate. The signal at δ 2.4 can be attributed to the allylic protons on carbon atoms C-1 and C-4 as part of the *trans* double bonds of PNBE and the signal at δ 2.9 is due to the allylic protons on C-1 and C-4 carbons as part of the *cis* double bonds of PNBE. The peaks at δ 1.1, 1.4 and 1.9 are due to the protons of carbons C-5, C-6 and C-7. The protons attached to atoms C-2 and C-8 due to the *cis* double bonds in PNBE appear at δ 5.2 and the *trans* double bond protons appear at δ 5.4. These signals are characteristic of the ring-opened units of PNBE. However, the protons on C-2′ and C-3 could not be seen in the spectrum at room temperature. This is the first time such an NMR study has been carried out using an ill-defined, in situ-generated catalyst. The pattern of NMR obtained for the propagating species is ostensibly similar to that observed by Gilliom and Grubbs [9] with a well-defined initiator (inset Fig. 2). A comparison of the spectral details between these two systems is shown in Table 2 and it can be seen that these spectra compare very well with each other except for the signal of the proton on the C-2′ carbon, which is not seen in our system. A similar spectral pattern for the ROMP reaction by a well-defined initiator was reported by Matyjaszewski and co-workers [10]. These results unequivocally confirm the presence of a metal carbene at the end of the polymer strands in our system.

The ‘quasi living’ nature of this metathesis catalyst was obtained by synthesis of block copolymers from end-capping and linking reactions with aromatic aldehydes. Thus the active species, generated as detailed before, was used for polymerising PA and the resulting living polymer (PPA) was reacted with terephthalaldehyde to give polymer with one aldehyde end group. A portion of it was precipitated in methanol, washed, dried and characterised by ^{1}H-NMR, which showed a peak at 10.1 ppm confirming the presence of an aldehyde end-group in the polymer chain. The molecular weight of this polymer was determined using GPC. The end-capped PPA was then reacted with polynorbornene (PNBE) with ‘active end’ to give a block copolymer containing *p*-phenylene as the linking unit. The block polymer was characterised by spectroscopic techniques and the molecular weight of the polymer was determined by GPC. The results of these experiments are summarised in Table 3. A similar experiment was carried out by end-capping PNBE and reacting it with ‘active’ PPA (Scheme 1).

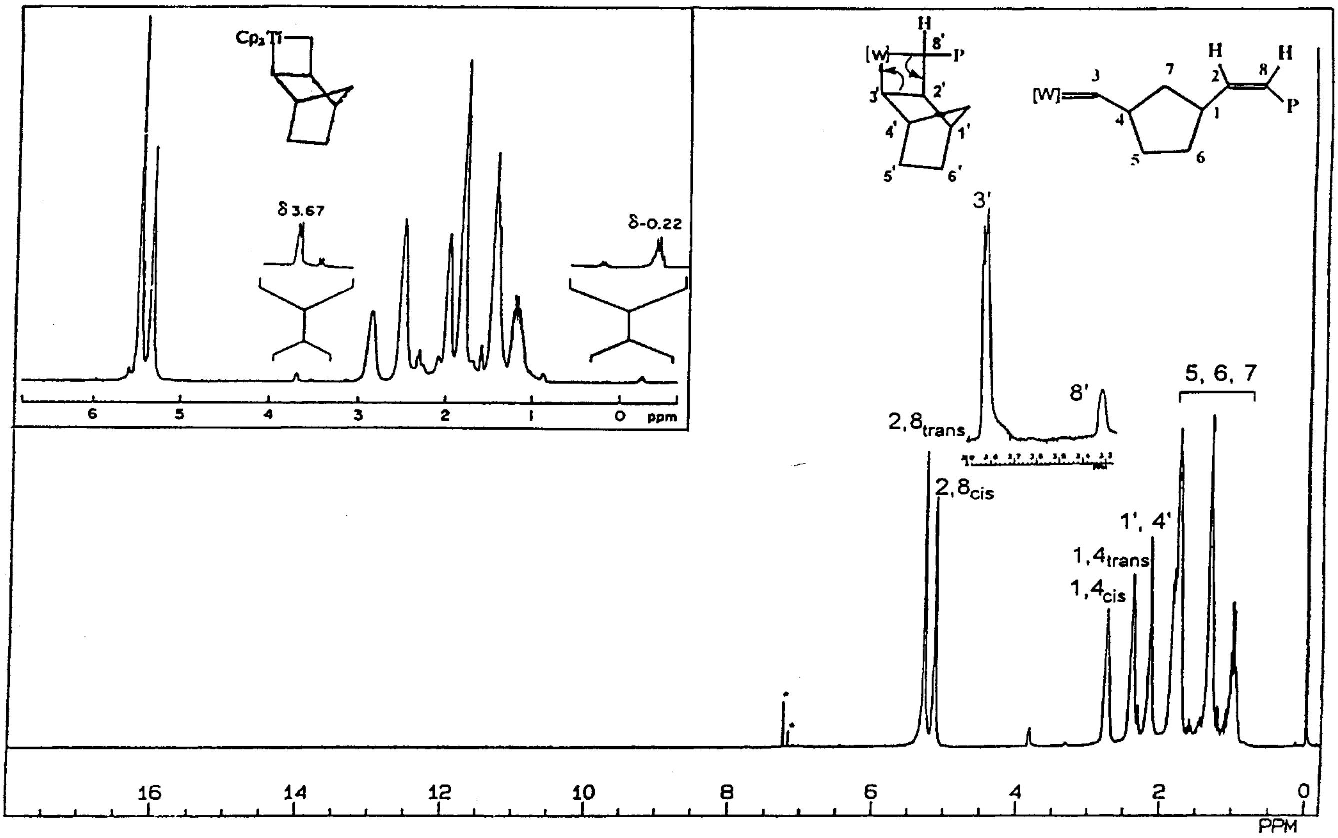


Fig. 2. ^{1}H-NMR spectrum obtained 1 h after addition of NBE to active species (signals marked by asterisk are solvent peaks).

The GPC curves for the homoPPA, end-capped PPA and p-phenylene linked PPA-PNBE copolymers are shown in Fig. 3. Since 50 equivalents of PA and 50 equivalents of NBE were taken in these experiments, the expected molecular weight of the p-phenylene linked block copolymer is around 10 100. The M_n values of the copolymer products were comparable, thereby providing evidence for the living nature of the polymer generated from this system.

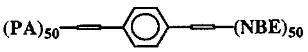
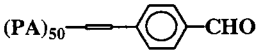
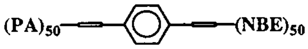
4. Conclusions

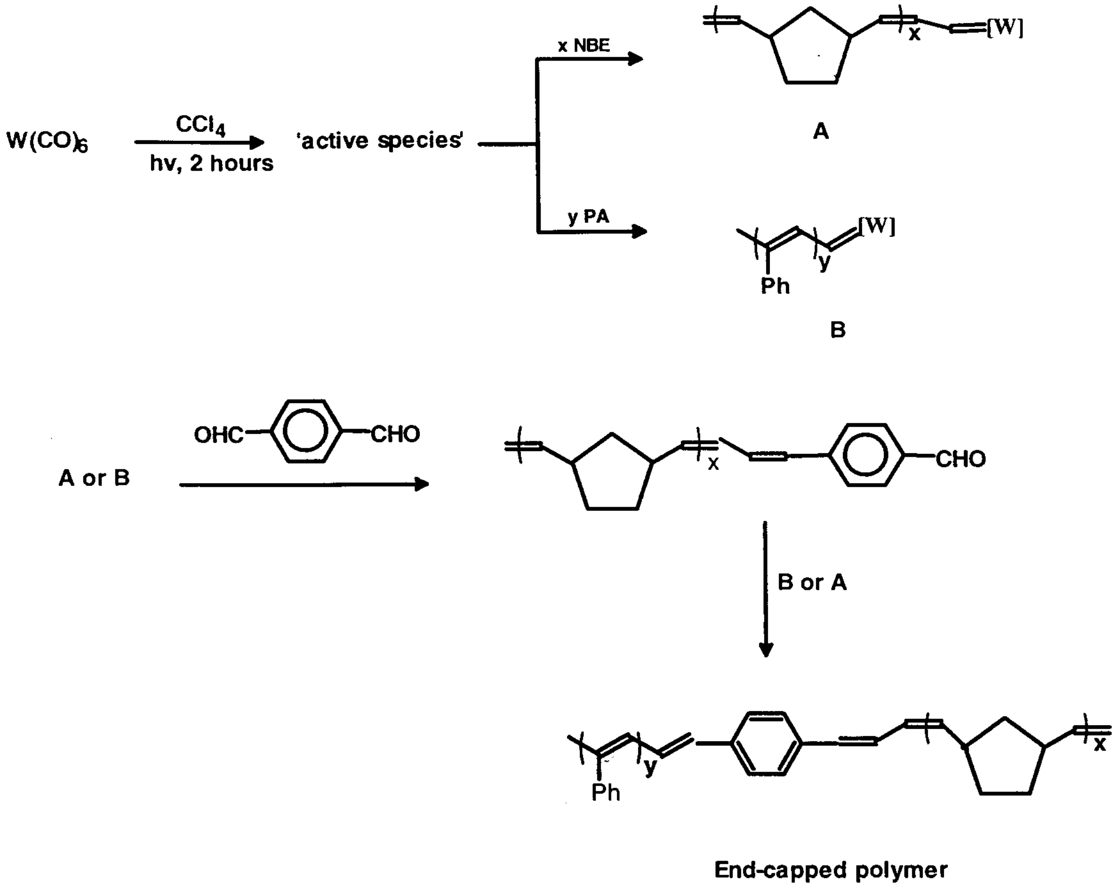
From the results given above we conclude that the precipitate formed after 2 h of irradiation is active for the polymerisation of phenylacetylene and norbornene. Once the monomers are added, the precipitate starts driving the polymerisation reaction and it is believed to contain carbonyl and chlorine ligands around the tungsten centre as well as the essential metal carbene unit. Further attempts to characterise the active species are in progress.

Table 2
Comparison of chemical shift values of protons for the adduct of NBE with the active species in $W(CO)_6/CCl_4/h\nu$ system with those of a similar adduct reported in Ref. [9]

Protons attached to carbons	δ (observed)	δ (reported) [9]
Signals due to the metallacyclobutane		
C-3′ and C-8′	3.8 (d) and 3.3	3.7 (d) and 3.4
C-1′ and C-4′ (bridge head protons)	2.1	2.2
C-2′	Not seen	−0.22
Signals due to ring-opened polymer		
C-2 and C-8 olefinic protons		
(a) of *trans* double bonds	5.4	5.4
(b) of *cis* double bonds	5.2	5.2
C-1 and C-4 allylic protons		
(a) of *trans* double bonds	2.9	2.9
(b) of *cis* double bonds	2.4	2.5
C-7	1.9	1.9
C-6	1.4	1.4
C-5	1.1	1.2

Table 3
Molecular-weight details of the end-capped PPA and the *p*-phenylene linked copolymers obtained from GPC studies of the end-capping reaction

GPC Trace (Fig. 3)	Polymer	M_n (expected)	M_n (observed)	M_w (observed)	M_w/M_n
A	$(PA)_{50}$	5200	5700	7200	1.26
B		10100	11200	14200	1.29
C		5300	5700	7400	1.29
D		10100	11200	14300	1.27



Scheme 1. End-capping of polymers with terephthalaldehyde.

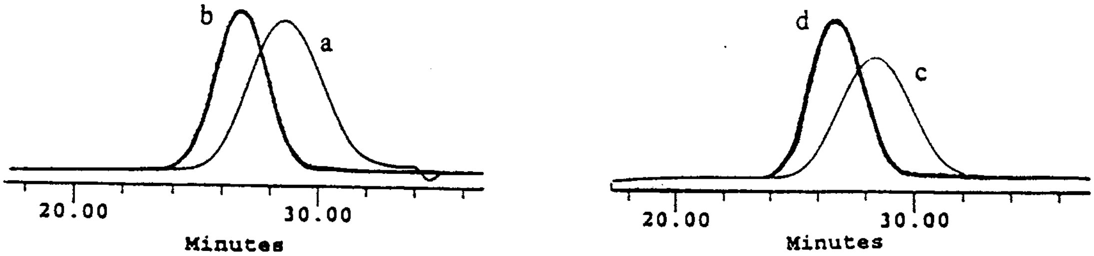


Fig. 3. GPC curves of (a) PPA; (b) *p*-phenylene linked copolymer of PNBE and PPA; (c) PPA end-capped with terephthalaldehyde; (d) *p*-phenylene linked copolymer of PPA and PNBE.

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